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A STUDY OF THE Pb PRECIPITATION IN NaCl FROM THERMAL CONDUCTIVITY EXPERIMENTS

M. Locatelli, R. Suchail and E. Zecchi*

Service des Basses Températures, Laboratoire de Cryophysique, Centre d'Etudes Nucléaires de Grenoble, 85 X, 38041 Grenoble Cedex, France

**Gruppo Nazionale di Struttura della Materia CNR, Istituto di Fisica dell'Universita di Parma, Italy*

Abstract. - Phonon interactions are very useful in the study of large defects in dielectric crystals. We present here the study of the nucleation phenomenum of Pb in NaCl by means of thermal conductivity experiments between 50 mK and 50 K, and give some elements in favour of the hypothesis that the vacancy is the scattering center in the IV dipole (Pb^{2+} vacancy) phonon interactions.

1. Introduction - The interaction of phonons with large defects in dielectric crystals depends on the characteristics of the defect (dimensions, shape, density) and on the phonon frequency (1). Therefore thermal conductivity experiments can be very useful in the study of such defects. Since phonons interact with many different defects, it is necessary to know the different interaction processes available in the studied system, in order to analyse the results.

In previous work (2) on Pb nucleaction in KCl we have deduced the presence of a cylindrical Suzuki like phase ($PbCl_2$ superlattice), also we have observed phonon scattering by I.V. (Pb^{2+} vacancy) dipoles and formulated the hypothesis that the scattering center is the vacancy, as the resonance frequency does not depend on the cation (3).

It is interesting to confirm this hypothesis and in order to do this we have studied by the same technique the NaCl : Pb system, where the site of the vacancy is different from that in KCl : Pb (4).

2. Experiments and Results - All the samples were provided by Prof. R.CAPELLETTI from Parma University (Italy) and their characteristics are given in Table I.

The thermal conductivity has been measured by the standard method in two thermal states for the doped crystals : as received and quenched. The thermal treatment at 500°C for two hours before quenching to LNT permits to dissolve some of the large defects.

I.V. dipole concentration in the different states and samples has been measured using Ionic Thermo Currents (ITC) technique by the Parma Group. A pure NaCl sample has been measured too as a reference.

The results are shown in Fig.1, and we can make the following remarks : i) for the heavily doped sample it is impossible to dissolve all the lead by a quenching this result is confirmed by ITC too, ii) for the sample with the lightest doping, the "dip" at high temperature, attributed to I.V. dipoles, is very small, while ITC experiments show the presence of I.V. dipoles.

3. Quantitative Analysis - We use the Debye model, as employed in (5), to analyse the results : in this model the different scattering processes are considered independent and the total inverse relaxation time is given by the relation :

$$\tau^{-1} = v/b + G\omega + A\omega^4 + \tau^{-1}_{ph\ ph} + \Sigma\ \tau_i^{-1}$$

v/b, $G\omega$, $A\omega^4$ and $\tau^{-1}_{ph\ ph}$ correspond to the boundary, dislocation, point defect and phonon phonon scattering, v is the sound velocity, b the sample dimension ; only G and A can vary with the thermal state of the sample.

$\tau^{-1}_{ph\ ph}$ has been accurrately determined using the results for the pure sample :

$$\tau^{-1}_{ph\ ph} = 84370\ \omega^2\ T \exp\ (-\ 310/4.5 \times T)$$

τ_i^{-1} are related to the IV dipole and large defect scattering.

The following expressions have been used :

- IV dipole $\tau^{-1}_{IV} = D\omega^4 / (\omega^2 - \omega_0^2)^2$ elastic scattering where D is proportional to the IV concentration and ω_0 is the resonance frequency,
- large defects : two types
  . Spherical $\tau_r^{-1} = N_r\ v^{-1}\ \sigma_r$ where N_r is the spherical defects concentration

$$\sigma_r = \Pi\ r^2 \times \begin{cases} (1 + R \exp(-\frac{1}{3})) \times (r\omega/v)^4 & \text{for } \frac{2r\omega}{v} < 1.5 \\ (1 + R \exp(-\frac{r\omega}{3v})) & \text{for } \frac{2r\omega}{v} > 1.5 \end{cases}$$

  where r is the radius of the defect and R a scattering efficiency coefficient.

  . Cylindrical $\tau_{\ell d}^{1} = N_{\ell d}\ v^{-1}\ \sigma_{\ell d}$ where $N_{\ell d}$ is the cylindrical defects concentration and $\sigma_{\ell d} = \sigma_d + \sigma_e$

$$\text{with}\quad \sigma_\ell = gV^2\ (\omega/v)^3 \text{ for } \ell\omega/v < 1.5$$
$$= gV^2\ (\omega/v)^3 \exp\ (-c(\frac{\omega}{v} - \frac{1.5}{\ell})^2) \text{ for } \frac{\ell\omega}{v} > 1.5$$
$$\sigma_d = fd\ell\ (d\omega/1.5v)^4 \text{ for } d\omega/v < 1.5$$
$$= fd\ell \quad \text{for } d\omega/v > 1.5$$

  where ℓ is the length, d the diameter and V the volume of the cylinder, v the sound velocity, g, f are scattering efficiency coefficients, c an adjustable parameter.

The values of the main parameters corresponding to the curves in Fig.1 are given in the Table 1.

We note that the fits are good for the heavily doped sample, but not excellent for the two other samples. This can be attributed to the presence of impurity ions which modify the thermal conductivity mainly for the undoped or lightly doped sample.

Nevertheless we can deduce the following results from the analysis i) the lead nucleaction gives rise to large defects with the dimension and shape depending on the Pb concentration : spherical at low concentration and cylindrical at high concentration.

ii) the IV dipole phonon scattering is weak and corresponds to a resonance temperature of 55 K.

This behaviour is different from the one observed in the KCl : Pb system where the scattering is stronger and at a resonance temperature of 29 K.

4. Conclusion - The scattering center in the IV dipole phonon interaction seems to be the vacancy, and a quantitative model will be developed in the future.

Moreover the Pb nucleaction gives rise to large defects where the shape, spherical or cylindrical, seems to depend on the Pb concentration.

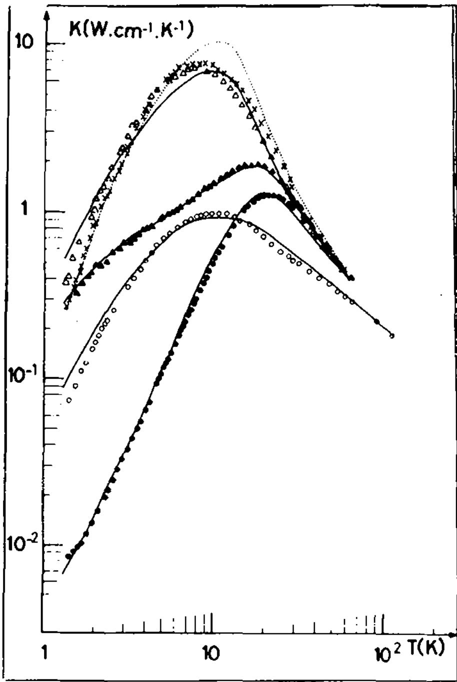

Fig.1 - Thermal conductivity versus the temperature for symbols see. Table 1

SAMPLE Pb conc.	1 210 ppm	1 210 ppm	2 50 ppm	2 50 ppm	3 PVR
Fig. SYMBOL STATE	● As received	○ Quenched	▲ As received	Δ Quenched	× As received
$T_o \xrightarrow{K} \omega o$		55		55	
D(a.u)		2.10^9	0	2.10^8	0
$N_{\ell d}$ (a.u)	12	.3	0	0	0
ℓ (Å)	100	100			
d(Å)	17	17			
N_r (a.u)	0	0	.3	0	
r(Å)			11		
A (a.u)	10	10	10	10	10
G (a.u)	0	0	0	0	0

Table 1

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